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Electropolymerization of Microencapsulated 3-hexylthiophene for Lithium-Ion Battery Applications

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The conductive polymer precursor, 3-hexylthiophene (3-HT), is successfully encapsulated in ca. 5 μm polyamide microcapsules by interfacial polymerization. The microcapsules are thermally stable up to 300°C, and electrochemically stable in a Li-ion battery electrolyte. Mechanical rupture of the microcapsules releases the liquid core and electropolymerization of the 3-HT monomer was analyzed using cyclic voltammetry. Scanning electron microscopy and vibrational (Raman) spectroscopy confirm the presence of newly formed poly(3-HT) thin films on model electrode surfaces. Encapsulation of battery additives such as 3-HT in microcapsules that remain latent and stable in the electrolyte until required may lead to enhanced battery performance and extended battery lifetimes.
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The use of electrolyte additives such as electrode stabilizers,[1–3] electrolyte stabilizers,[4] and flame retardants[5–7] has led to significant improvements in battery performance and safety. However, in many cases additives degrade secondary properties such as ionic conductivity of the electrolyte, cell impedance, or electrode irreversibility, particularly if the amount of additive in the electrolyte is more than 5% by weight or volume.[8,9] Thiophene derivatives (e.g. 3-HT) have garnered attention recently as life-extending additives for Li-ion batteries.[10,11] The 3-HT monomer forms a stable, conductive, passivation layer upon oxidation on the cathode surface, and has been shown to improve performance in Li-ion half cells with both high-capacity and high-voltage cathodes by reducing interfacial impedance, increasing thermal stability, and serving as a protective barrier against destructive agents, such as HF.[11] Although some thiophene derivatives form beneficial conductive membranes on a cathode surface, their prolonged presence in the battery electrolyte leads to a degradation of Li-ion battery performance.[9]

Microencapsulation is an effective strategy for sequestering a reactive core material from the environment and provides an alternative approach to the direct incorporation of battery additives into the electrolyte. Timed or triggered release of battery additives from a microcapsule[12] has the potential to deliver the proper dosage of the additive over the lifespan of the cell, whereas direct addition into the electrolyte results in full consumption of the additive within the first few cycles[13] or a harmful excess leading to decreased electrode performance.[10,14] For example, the additive vinylene carbonate (VC)[1,15] forms a stable, solid electrolyte interphase (SEI) layer on the anode surface during the first few cycles, but any excess VC in the electrolyte decomposes at the cathode during elevated temperature storage.[16–18]

Triggered release of battery additives may prove to be a more effective approach to battery design. Active particles in $LiCoO_2$,[19,20] $LiMn_2O_4$,[21–23] and $LiFePO_4$ [24] cathodes may crack after prolonged cycling and subsequently reduce cathode conductivity. Previous attempts to alleviate this problem involve doping battery electrodes with conductive polymer particles.[25,26] The incorporation of microcapsules containing 3-HT monomer into battery cathodes would enable localized (site specific) core delivery to cracked cathode particles triggered via mechanical rupture of the capsule shell wall.

Here, we describe the encapsulation of 3-HT monomer in polyamide microcapsules for incorporation into battery cathodes. The shell wall insulates the monomer core from electropolymerization until the microcapsule is mechanically crushed, locally releasing the monomer core. The released 3-HT monomer is polymerized to form poly(3-HT) films on model battery electrodes during cyclic voltammetry.

Experimental

Particle size measurements for the 5 μm microcapsules were obtained using a Particle Sizing Systems AccuSizer FX instrument. The particle size distribution was determined by measuring the extinction of a focused laser beam in a dilute dispersion of microcapsules in water flowing through a detection volume.

Thermal gravimetric analysis (TGA) was carried out on a Mettler-Toledo TGA/DSC. Data was collected in the range of 25°C–650°C with a heating rate of 10°C min^{-1} under a dry nitrogen atmosphere.

^1H NMR spectra were obtained with a Varian 500 MHz spectrometer in the School of Chemical Sciences NMR laboratory at the University of Illinois at Urbana-Champaign. Chemical shifts are reported in δ (ppm) relative to the $CDCl_3$ solvent peak.

Cyclic voltammetry experiments were performed in a one-compartment three-electrode electrochemical cell with an Al working electrode, a Li reference electrode, and a Li counter electrode using an Arbin B200 instrument with a sweep rate of 10 mV s^{-1} in an Argon-filled glove box.

Scanning electron microscopy (SEM) samples were obtained after rinsing microcapsule-coated electrodes in methanol after CV. SEM images and Energy Dispersive X-ray Spectroscopy (EDAX) data was taken using a Philips XL30 ESEM-FEG environmental SEM after sputter coating the cathodes with a gold/palladium target.

Raman spectroscopy was conducted using a Horiba LabRAM HR 3D-capable Raman spectroscopy imaging system microscope with a 20× objective. For each sample, measurements were collected using a 785 nm excitation source with a 1 sec acquisition time per measurement.

Results

Microcapsule preparation and characterization.— Microcapsules containing 3-HT monomer were prepared by interfacial polymerization of terephthaloyl chloride and diethylenetriamine (DETA) following the encapsulation procedure shown in Figure 1, as modified from the scheme described by Mathiowitz et al.[27] and Pastine et al.[28] A surfactant solution of ethylene maleic anhydride (EMA) and water was first prepared and homogenized at 4000 rpm. The homogenizer

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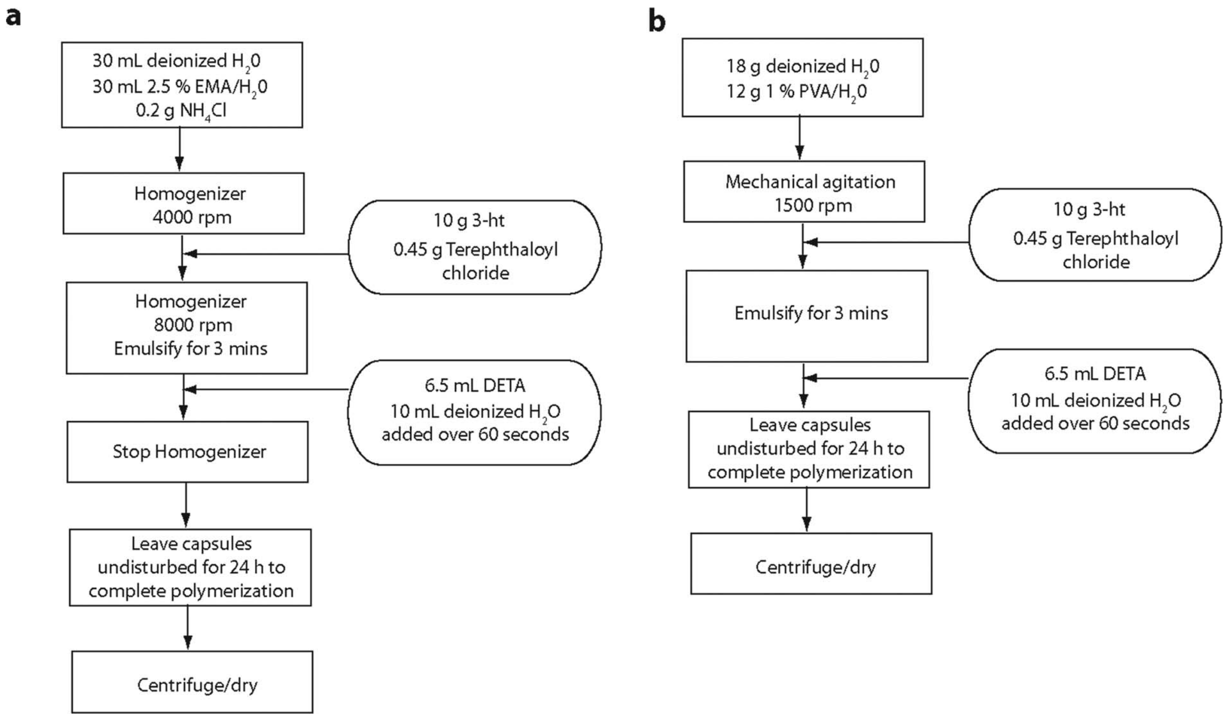

Figure 1. Microencapsulation procedures for polyamide microcapsules containing 3-hexylthiophene. (a) Procedure for ca. 5 μm capsules, (b) Procedure for ca. 178 μm capsules.

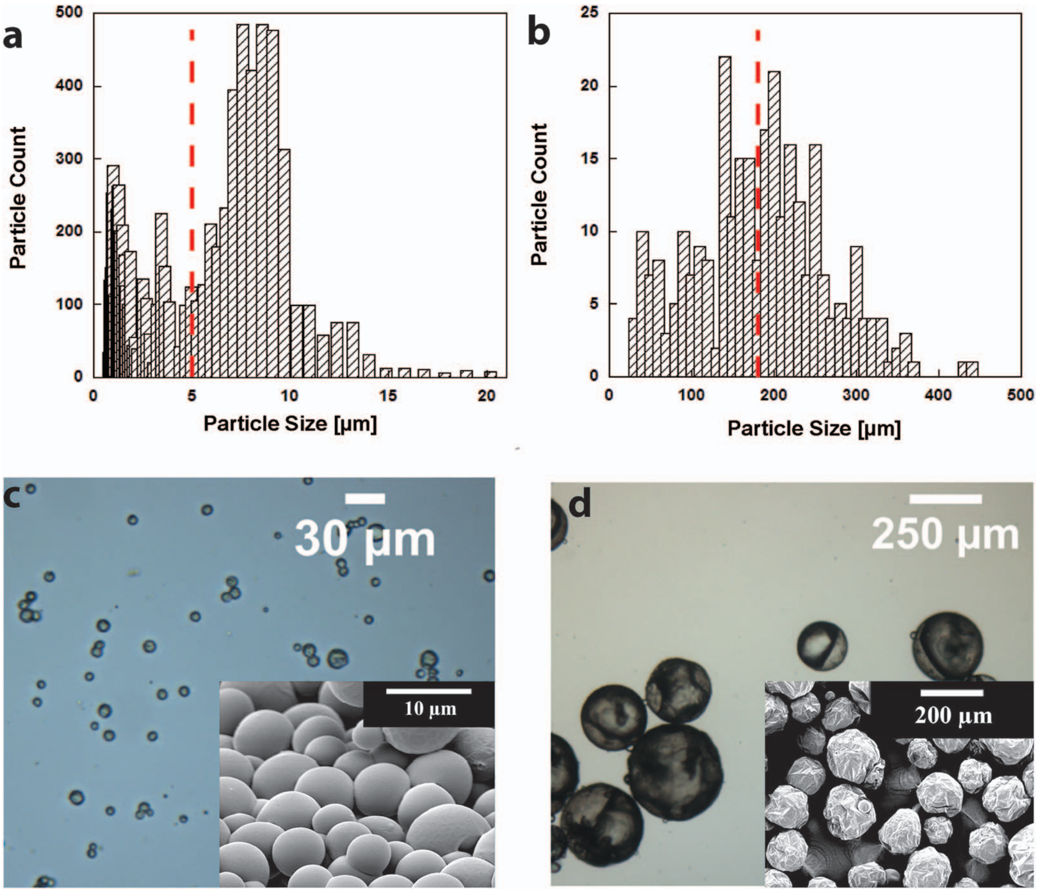

Figure 2. Characterization of polyamide microcapsules containing 3-HT monomer. (a) Size distribution of homogenized microcapsules prepared according to Fig. 1a. The dashed line indicates the average microcapsule diameter. (b) Size distribution of homogenized microcapsules prepared according to Fig. 1b. The dashed line indicates the average microcapsule diameter. (c) Optical image of small 3-HT microcapsules in water and (inset) SEM image showing smooth surface morphology. (d) Optical image of large 3-HT microcapsules in water and (inset) SEM image showing rough surface morphology.

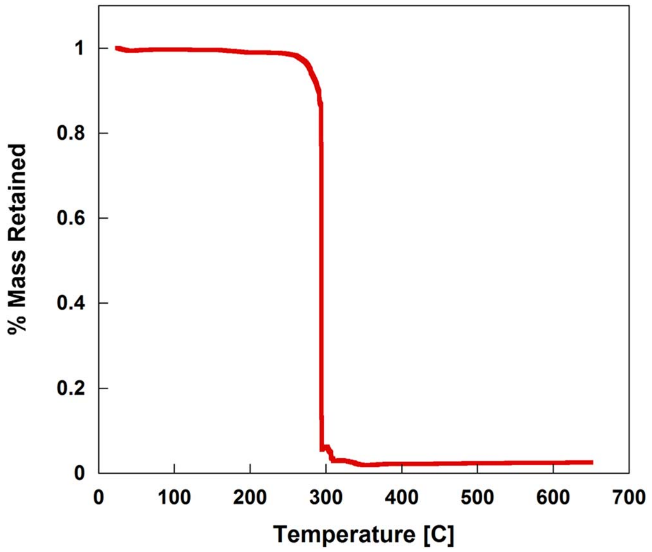

Figure 3. TGA trace of small (ca. 5 μm diameter) polyamide microcapsules containing 3-HT.

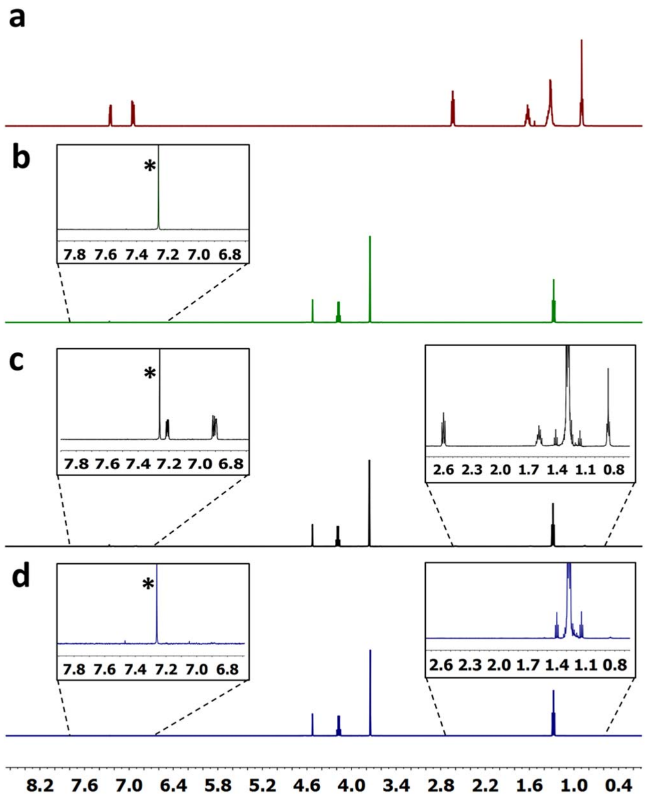

Figure 4. ^1H NMR spectra (in $CDCl_3$) of (a) neat 3-HT monomer, (b) neat electrolyte, (c) a reference sample consisting of 5 wt% 3-HT added into electrolyte, and (d) electrolyte solution isolated from 3-HT microcapsule/electrolyte sample. The peak marked with (*) is residual $CHCl_3$ in $CDCl_3$.

speed was then increased to 8000 rpm and the core solution consisting of terephthaloyl chloride powder and 3-HT was emulsified for 3 min in the surfactant solution. A solution of DETA in H_2O was then added to the emulsion initiating a reaction with terephthaloyl chloride and resulting in polymeric wall formation around the 3-HT core droplets.

Membrane formation around the oil droplets was nearly instantaneous, but the microcapsules were left undisturbed for 24 hours to complete the polymerization and ensure that solid-walled and impermeable microcapsules were obtained. The microcapsules were then centrifuged to remove excess surfactant and freeze dried for 24 h to produce robust, liquid-filled microcapsules. Microcapsules produced by this procedure have an average diameter of 5 μm and a bi-modal distribution as shown in Figure 2a. The microcapsules have a smooth outer shell wall and are free flowing, as revealed by optical microscopy (Figure 2c). Key changes in this encapsulation procedure from that described in prior literature are the use of EMA surfactant and the addition of NH_4Cl to better stabilize the emulsion and enable formation of small diameter microcapsules suitable for Li-ion battery applications.

Larger microcapsules were also prepared following the modified procedure in Figure 1b. The resulting microcapsules have an average diameter of 178 μm, as shown in Figure 2b. Their shell wall morphology is significantly rougher than the smaller, 5 μm microcapsules (Figure 2d). The ratios of shell to core for our microcapsules are approximately 1:3 and 1:12 for 5 μm and 178 μm capsules, respectively.

Microcapsules designed for Li-ion battery applications must remain stable at temperatures of approximately 60°C, the upper end operating temperature of a Li-ion battery cell.[29,30] Thermal gravimetric analysis (TGA) was used to examine the thermal stability of ca. 5 μm dried 3-HT microcapsules. As shown in Figure 3, the microcapsules remain stable to approximately 300°C, at which point the polyamide shell wall degrades. The sharp drop in mass loss upon shell wall rupture in the TGA trace is consistent with literature results for other polyamide microcapsules.[31]

Stability of microcapsules to electrolyte exposure was investigated by ^1H nuclear magnetic resonance (NMR) spectroscopy. Rinsed, freeze dried microcapsules (5 wt%) were added to a commercial electrolyte of 0.1 M $LiClO_4$ in 1:3 ethylene carbonate (EC): dimethyl carbonate (DMC). Microcapsules were stored in a sealed vial of electrolyte for 4 weeks in an Argon-filled glove box. After 4 weeks, the mixture was centrifuged to isolate microcapsules from the electrolyte, and an aliquot of electrolyte was dissolved in deuterated chloroform for ^1H NMR analysis. Compared to the spectra of neat 3-HT monomer and of the neat electrolyte, no monomer was observed in the electrolyte solution, indicating that the core material did not diffuse through the microcapsule shell wall (Figure 4).

Electropolymerization of 3-hexylthiophene.— The in situ electropolymerization of 3-HT monomer released from microcapsules was characterized through cyclic voltammetry of model battery electrodes. Cyclic voltammograms were recorded at 10 mV s^{-1} over a 2–5 V voltage window using an Al foil working electrode and Li metal counter and reference electrodes immersed in electrolyte. A slurry containing 1.5 wt% 3-HT monomer filled microcapsules in water was applied to a 1 mm × 2 cm strip of cleaned battery-grade Al foil followed by drying in air overnight.

As controls, we performed cyclic voltammetry on neat electrolyte and on 1.5 wt% 3-HT monomer added directly to the electrolyte. The first cycle of the cyclic voltammogram trace for each sample was selected for analysis and compared in Figure 5. The voltammetry sweep on the neat electrolyte shows no voltage peaks indicating that the electrolyte is electrochemically stable and inert within the 2–5 V voltage window. Oxidative electropolymerization of 1.5 wt% 3-HT monomer is apparent at approximately 4.5 V vs. Li in the voltammetry sweep of 1.5% 3-HT monomer added directly to the electrolyte. For older-generation battery materials, such as $LiCoO_2$/graphite, indeed, the 3-HT monomer oxidizes above the end-of-charge potential of $LiCoO_2$, so polymer formation requires overcharging. In contrast, modern cathodes such as $Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$, and $LiNi_{0.5}Mn_{1.5}O_4$ require charging to 4.0 V or higher,[11] which is ideal for polymerizing 3-HT. The electropolymerization of 3-HT is not reversible as evidenced by the lack of a peak on the cathodic scan (reverse trace) from 5 V to 2 V.

Al foil samples coated with 178 μm microcapsules containing 3-HT were first tested to verify that the monomer was electrochemically isolated from the polymerizing voltage. No polymerization peak was present in the initial voltammetry trace, confirming the effectiveness of the capsules in achieving electrical insulation. Samples were

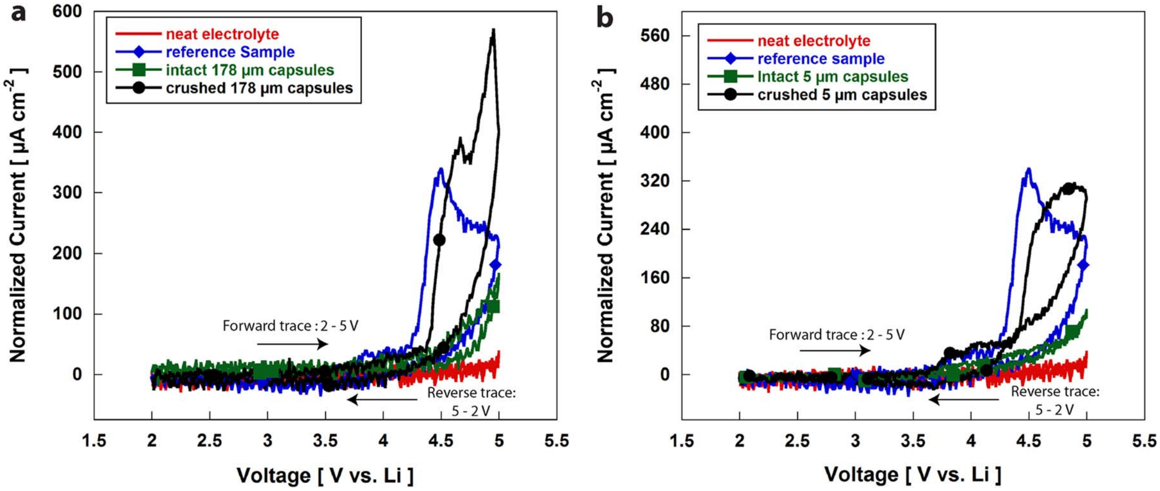

Figure 5. First cycle of cyclic voltammetry traces for model electrodes. (a) Samples containing large (178 μm) 3-HT microcapsules and controls. (b) Samples containing small (5 μm) 3-HT microcapsules and controls. Note: Neat electrolyte signifies electrodes with $LiClO_4$ EC:DMC electrolyte only (no microcapsules). Reference sample indicates 1.5 wt% 3-HT added to electrolyte directly (no microcapsules).

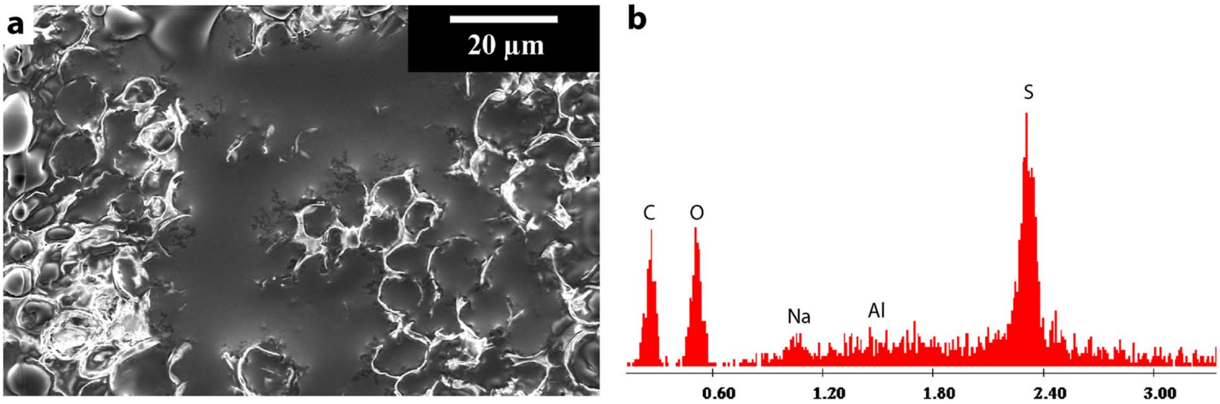

Figure 6. SEM and EDAX characterization of the electropolymerized poly(3-HT) film from 5 μm microcapsules. (a) SEM image of polymer film that forms after electropolymerization of 3-HT monomer released from ruptured microcapsules. (b) EDAX spectrum indicating presence of sulfur in the polymer film.

then removed from electrolyte and pressed between two glass slides to visibly rupture the microcapsules and release the core 3-HT monomer. Cyclic voltammetry was repeated and a new current peak appears at a voltage of 4.6 V, slightly above the polymerization voltage of 3-HT, indicative of polymer formation. This slight overpotential is likely due to the presence of insulating polymer microcapsule shell wall fragments. Al foil samples coated with 5 μm microcapsules containing 3-HT were tested using a similar procedure, although a cryofracture technique was used to embrittle the shell wall and aid in mechanical crushing.

Polymer characterization.— The electropolymerized poly(3-HT) films were rinsed with methanol and then examined using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDAX), and Raman spectroscopy. SEM imaging reveals a thin film covering the surface of broken microcapsules (Figure 6a). EDAX on the thin film shows a distinct sulfur peak, which is attributed to poly(3-HT) (Figure 6b). The poly(3-HT) film is easily damaged by SEM and Raman spectroscopy, suggesting that the film is very thin.

These polymer films were also analyzed by Raman spectroscopy (Figure 7) to verify the existence of poly(3-HT) as opposed to residual monomer. The Raman spectrum displays a band of intensity from 1300–1500 cm^{-1} as well as several secondary peaks (750 cm^{-1}, 1000 cm^{-1}, 1090 cm^{-1}, 1200 cm^{-1}) that are indicative of poly(3-HT). These peaks correspond to the various stretching and bending vibrational modes found only in poly(3-HT) and not 3-HT monomer.[32] To confirm, we collected Raman spectra of both neat 3-HT monomer as well as a reference sample of 1.5 wt% 3-HT monomer added directly to the electrolyte and polymerized by CV from 2–5 V. Distinct absorbance peaks at 940 cm^{-1} and 1500 cm^{-1} for the 3-HT monomer are absent in both the reference and ruptured capsules samples. As a further control, a Raman spectrum of the neat electrolyte was also collected (red curve), to provide confirmation that the methanol rinsing and drying steps removed the electrolyte in the sample preparation process.

Conclusions

3-hexylthiophene, a Li-ion battery additive known to improve high-voltage cathode performance, was successfully encapsulated in polymeric microcapsules. The microcapsules electrically insulate the monomer until the microcapsules are ruptured. Once the microcapsules release their payload, the monomer is electrically polymerized to form a thin poly(3-HT) film. The microcapsules are stable to 300°C, compatible with $LiClO_4$ EC:DMC electrolyte, and mechanically robust, allowing them to be coated on an electrode surface or potentially incorporated into an electrode slurry. SEM images confirm the formation of a thin film in the vicinity of ruptured microcapsules, which was characterized as poly(3-HT) by Raman spectroscopy. While prior attempts to encapsulate battery additives have been made,[33] this work describes the first demonstration of an electrolyte-stable, microencapsulated Li-ion battery additive. However, mechanical rupture was

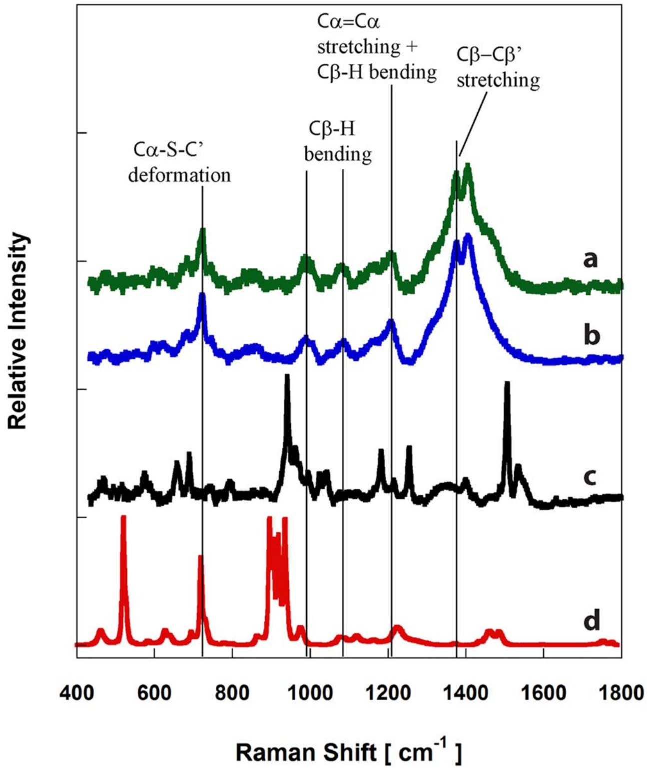

Figure 7. Raman spectra of poly(3-HT) film formed by electropolymerization by CV of 3-HT monomer released from microcapsules together with controls. (a) Microcapsule sample, (b) reference sample of 1.5 wt% 3-HT monomer added directly to electrolyte, (c) neat 3-HT monomer, and (d) neat electrolyte.

required for delivery of the core additive. In the future, programmable capsules,[34] that trigger in response to voltage may prove useful for autonomous delivery of a variety of battery additives for improved and more stable long-term performance.

Acknowledgments

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